

Structural Changes in High-rank Bituminous Coals Caused by Solvent Swelling and Heat

Yongseung Yun and Eric M. Suuberg
Division of Engineering, Box D
Brown University, Providence, RI 02912

(Key Words: Bituminous coal structure, Solvent swelling, Differential Scanning Calorimetry)

INTRODUCTION

High-rank coals (>86 %C daf) have been known to exhibit fundamentally different response characteristics to heat and solvent treatments than lower-rank coals (< 86 %C daf). Sakurovs et al.[1] reported that heat is more effective than pyridine for creating mobility in coal structure, for coals of 86-90 %C daf. Also Iino et al.[2] showed that extraction yields using solvent mixtures of CS₂/N-methyl-2-pyrrolidinone(MP) (1:1 v/v) increase with carbon content up to 86 %C daf and then fall rapidly with further increase in carbon content.

High-rank coals do not significantly swell in pyridine, while most lower-rank coals show a substantial amount of swelling in that solvent. However, some combinations of solvents, especially with CS₂, yield for the higher-rank coals similar swelling ratios as can be obtained in lower-rank coals. The work of Iino et al.[2-4] is especially noteworthy, since they first reported the benefit of mixing CS₂ (which is a known good solvent for fats, resins, and rubbers) with several solvents (i.e., pyridine, dimethylsulfoxide, dimethylformamide, dimethylacetamide, MP), in enhancing extraction yield and volumetric swelling of coal, particularly around 86 %C daf.

It has also been demonstrated that the structure of high-rank bituminous coals can be thermally loosened, to yield high volumetric swelling ratios in pyridine (when the coals are heated to above 350°C)[5,6]. These swelling ratios are similar to those which can be obtained at room temperature in mixtures of CS₂/pyridine, CS₂/dimethylsulfoxide, or CS₂/dimethylformamide as will be shown in this paper.

In order to understand the underlying structural changes caused both by mixed solvents and heat, as well as to explore possible effective pre-liquefaction strategies for these high-rank bituminous coals, two coals, viz., Upper Freeport (mvb) and Pocahontas No. 3 (lvb), were studied using differential scanning calorimetry (DSC) and solvent swelling techniques.

EXPERIMENTAL

Aliquots of several coal samples, obtained from the Argonne National Laboratory - Premium Coal Sample Program, were analyzed by DSC and solvent swelling techniques. These samples included Illinois No. 6 (-20 mesh), Blind Canyon (-20 mesh), Upper Freeport (-100 mesh), and Pocahontas No. 3 (-20 mesh) coals. They were used as-received. Detailed petrographic, chemical, and physical analysis data on these coals can be found elsewhere [7].

Differential Scanning Calorimetry A DuPont 2910 DSC system with a liquid nitrogen cooling accessory (LNCA-II) was employed in this study. The sample cell was operated under a nitrogen flow rate of 90 ml/min in order to keep the cell free of oxygen during measurement. Aluminum sample pans were used in an unsealed mode. This was done by just pushing down the

top sample pan cover gently onto the bottom pan containing the coal. Samples were initially isothermal for five minutes and then heated from 30°C at 8 °C/min or 10 °C/min. Typically 6-9 mg of sample was used in an experiment. Cooling of the cell between consecutive heating scans normally involved air convection in the heating assembly, but the sample itself was always kept under nitrogen.

Solvent Swelling Coal samples were placed in constant diameter tubes (3 mm i.d., ca. 5 cm long) and centrifuged at 7500 rpm for 3 min in a roughly 30 cm horizontal rotor (SAVANT HSC-10K high speed centrifuge), after which the initial height of the sample was measured by a caliper. The choice of 7500 rpm was rather arbitrary and selected only to be as high as could be comfortably tolerated by the equipment. Solvent was then added and stirred until a visual check showed the total submergence of coal in solvent. The stirring was repeated frequently (normally 3 times) during the first 30 min following solvent addition. At the desired measurement times, the sample tubes were centrifuged again (7500 rpm for 3 min), the swollen coal height measured, and the solvent replaced with the clean solvent. This assured that the concentration of extractable was not so high as to interfere with the measurement.

Samples (22-28 mg) for solvent swelling were prepared in the DSC at a heating rate of 8 °C/min under a nitrogen flowrate of 90 ml/min. After reaching the desired temperature, each sample was cooled immediately by contacting the bottom of the sample pan with ice or cold water. Swelling solvents employed were all reagent grade and were used without any further purification.

Sample Pretreatment In order to determine the main parameters governing the relaxation of coal structure, several treatments were performed before subjecting the samples to DSC or solvent swelling. These include preswelling by solvent, pyridine Soxhlet extraction, acetylation, and heat treatment. Solvent preswelling was performed in two ways. One method involved swelling coal samples in the constant diameter glass tubes, which were used in the normal swelling experiments described earlier. The swelling was performed in excess solvent at room temperature for about 3-4 days with frequent replacement of extract-laden solvent with fresh solvent. The samples were subsequently dried under vacuum (<30 inHg) at room temperature for about two days. Another approach involved Soxhlet extraction of samples with pyridine for about two days, until the color of pyridine in the extraction tube indicated no further extraction. Then the sample was washed with deionized water, filtered using a water aspirator, and dried under vacuum (<30 inHg) at room temperature for about two days. Thus in the first case the samples were swelled but not exhaustively extracted, whereas in the second case the samples were exhaustively extracted (as well as presumably being fully swelled). Acetylation of hydroxyls was accomplished by mixing coal with excess pyridine and excess acetic anhydride at room temperature for about three days, and then excess acetic anhydride was destroyed by reaction with water while excess pyridine was removed by washing the sample with water. The acetylated sample was subsequently dried under vacuum at room temperature for about two days.

RESULTS AND DISCUSSION

Figure 1 shows difference DSC spectra, solvent swelling ratios in pyridine and tetrahydrofuran (THF), and pyrolytic mass loss for the Upper Freeport and Pocahontas No. 3 coals. The mass loss curves indicate the total loss observed from individual samples heated at 8°C/min and then immediately quench-cooled from the specified temperature by contacting the bottom of the sample pan with ice or cold water. The mass loss around 100°C shows the loss of moisture (around 1% in each sample) and the upturn at around 300°C heralds the onset of pyrolytic weight loss. It is presently unclear at what temperature pyrolysis reactions actually begin in these samples, since the mass loss at near 300°C might include physical evaporation of small molecules, in a manner analogous to the loss of water at 100°C. This point will be further discussed below.

The solvent swellability of the raw Upper Freeport and Pocahontas No. 3 samples is very low, prior to heat treatment (see middle panels of Figure 1). Both exhibit a volumetric swelling ratio of roughly 1.1 in pyridine, prior to heat treatment. As we discussed in our earlier papers [5,6], heat treatment appears to irreversibly "relax" the coal structure somewhat, such that both swellability in pyridine and THF is greatly enhanced, as is also seen in Figure 1. The temperature at which increased swellability is first observed is around 300°C in both the Upper Freeport coal and the Pocahontas No. 3 coal, although it takes considerably higher temperatures to achieve maximum swellability in the latter.

As we earlier noted [5], such irreversible changes in swellability correspond with events observed by DSC (see the top panels of Figure 1). In both coals, the dramatic rise in swellability coincides with a significant endothermic peak in the DSC spectra. The spectra are shown as difference spectra, obtained by scanning through the same temperature range three times with the same sample. The first minus second and first minus third scan spectra show the peaks distinctly, centered at 350°C in the Upper Freeport coal and at around 425°C in the Pocahontas No. 3 coal. The peaks around 100°C involve moisture loss. The second minus third scans show the absence of these peaks, confirming the irreversibility of the processes.

Figure 2 shows the actual raw DSC spectra for the two coals of interest here, compared with two spectra for lower-rank bituminous coals. While somewhat less distinct in feature than the subtracted spectra of Figure 1, the curves in the top panel show the clear endothermic peaks at 350°C and 425°C for the Upper Freeport and Pocahontas No. 3 coals, respectively. Such distinct peaks are not visible in the spectra of the lower rank coals in the lower panel in Figure 2, in which water evaporation process (endothermic) is followed by a more or less straight DSC response curve corresponding to the heat capacity of coal, and then followed by thermal degradation process where a peak occurs in the exothermic direction, in part due to weight loss. What is notable from the top panel is that the endothermic peaks corresponding to the irreversible relaxation of the structures of the higher rank coals are well separated from the main pyrolysis events, seen as major disturbances in the DSC curves. The sharp peak into the exothermic direction in the Upper Freeport coal is mainly caused by the sudden expansion of sample volume, with the development of plasticity.

The above observations do not establish the nature of the events resulting in the endothermic peaks coinciding with the relaxation event in the high-rank coals. They might be reaction endotherms, occurring prior to the main pyrolysis reactions, or they could be physical events of an endothermic nature (such as "melting"). The fact that the events are irreversible does not necessarily rule out an explanation based on physical processes, since the coal obviously does not have to reassume the same physical form upon cooling as it had in the raw state. We believe that the events have a high probability of having physical origin, based upon other observations. First, the endothermic peaks for two high-rank bituminous coals are similar to the "hysteresis" peak normally occurring just after the glass transition temperature in stressed polymers [8]. The hysteresis peak is mainly caused by stress relief of the structure by heat, quite often observed in amorphous polymers, e.g., epoxies, polycarbonate, polystyrene. Second, we believe that the behavior of one of the coals in certain solvents supports the hypothesis of a physical process.

It has been noted [2-4] that higher rank bituminous coals show a remarkably high degree of extractability in mixtures of certain solvents with CS₂. The Upper Freeport coal shows a sharp increase in room temperature swellability in a mixture of pyridine and CS₂, as noted in Figure 3. There is no need to heat treat the coal to achieve significant swellability, which suggests that a physical relaxation of the structure is all that is involved. There is, of course, the possibility that CS₂ undergoes chemical reaction with the coal, cleaving similar numbers of bonds as are cleaved

during heat treatment, but there is no strong reason to believe that this should be so. Moreover, as the data of Figure 3 show, there is a maximum in swelling ratio for the 1:1 by volume mixture of pyridine and CS_2 . It would be difficult to understand why, if CS_2 is a chemically reacting agent, such a stoichiometry would be needed, when solvent is in large excess. We thus are led to the tentative conclusion that the CS_2 /pyridine mixtures are effective mainly because of specific solvent properties.

The fact that the CS_2 /pyridine mixture relaxes the coal structure in a manner similar to heat, is established in Figure 4. Treating the coal with CS_2 alone, pyridine alone, or chloroform/pyridine mixtures leaves intact the DSC peak, corresponding to the relaxation of the structure. The Upper Freeport coal treated in CS_2 /pyridine, however, no longer shows such a relaxation event at 350°C . The CS_2 /pyridine mixture is not nearly as effective a swelling agent for Pocahontas No. 3 coal as for Upper Freeport coal. This, too, is confirmed by the DSC which still records a significant relaxation event for the previously pyridine/ CS_2 treated Pocahontas No. 3 coal (see lower panel of Figure 4). Apparently this specific solvent combination is only effective for a certain range of ranks. This is consistent with the observations of Iino et al. [3].

There is nothing particularly unique about the choice of pyridine in mixture with CS_2 . As Iino et al. earlier showed [2,3], N-methyl-2-pyrrolidinone/ CS_2 mixtures are also effective. We have established, as Iino et al. noted, that CS_2 /dimethylsulfoxide(DMSO) and CS_2 /dimethylformamide are also effective mixtures (see Table 1). Thus the solvent pair need not even include a nitrogen base, since DMSO is not. All the effective solvents in CS_2 mixtures are, however, fairly good electron donors.

Pyridine was tried in admixtures with other solvents of similar solubility parameter to CS_2 , and with other solvents that could serve as effective electron acceptors (see Table 1). None of these other combination rivaled the ability of the CS_2 /pyridine mixture to swell the Upper Freeport coal. Of course, these solvents did not yet include particularly strong electron acceptors (strong acids) and work on this point continues.

Pretreatment of the coal by pyridine extraction has little effect on its subsequent behavior in CS_2 /pyridine (see Table 1). Pretreatment of the coal by acetylation does little to change the behavior of the coal with respect to swelling in CS_2 /pyridine mixtures. This means that the structure is not irreversibly expanded to a significant extent by the acetylation alone. This suggests that it is not, for example, a xanthate formation type of process [9-11] involving CS_2 and the hydroxyl groups in the coal that results in the greater swellability of the coal in CS_2 /pyridine mixtures. The completeness of our acetylation has not yet been established, so its conclusion is still tentative.

Pretreatment of the coal in CS_2 , followed by removal of the CS_2 by evaporation and then subjected to pyridine swelling, showed again the importance of the interaction of pyridine and CS_2 . The sequence resulted in pyridine swelling comparable to that of the raw untreated coal (see Table 2). Reversing the order of sequential exposure was also not effective (again see Table 2).

When the coal was "relaxed" by exposure to CS_2 /pyridine mixtures, it was more swellable than in the raw state, by either of these solvents (see Table 2). The fact that the swellability was not as great as that induced by the thermal treatment to 350°C is also seen in Table 2. This is because

once swollen in pyridine/CS₂ mixture, it is difficult to fully remove all of the pyridine from the coal by vacuum drying. Thus the coal is already in a partially swollen state, due to the irreversibly bound pyridine. Heating a CS₂/pyridine swollen coal to 350°C results in a higher subsequent pyridine swellability (relative to the vacuum dried CS₂/pyridine swelled coal), because the pyridine is fully lost upon heating.

Results of swelling by solvents for low volatile bituminous Pocahontas No. 3 coal (91.1 %C daf) are illustrated in Table 3. As can be expected from DSC responses for CS₂/pyridine-swollen Pocahontas No. 3 coal (see Figure 4), even CS₂/pyridine mixture was not as effective in swelling as for Upper Freeport coal. However, heat treatment up to 450°C can relax the coal structure enough to induce swelling of more than 60% by THF and pyridine. At present, only heat appears to be an effective agent for loosening the structure of low volatile bituminous coal significantly.

CONCLUSIONS

- Two high-rank bituminous (Upper Freeport: mvb, Pocahontas No. 3: lvb) coals exhibit a distinct endothermic DSC peak corresponding to the irreversible relaxation of the structure. The endothermic peaks are well separated from the main pyrolysis events and appear to originate from physical processes rather than from chemical reaction processes.
- Even strong solvents (e.g., pyridine) cannot swell the structure of high-rank coals more than ten percent at low temperatures (<250°C). Heat treatment above 300°C can enhance the swelling of both Upper Freeport and Pocahontas No. 3 coals significantly. Solvent swelling by mixtures of solvents (e.g., with CS₂) is effective in relaxing the structure of medium volatile bituminous Upper Freeport coal, but not for low volatile bituminous Pocahontas No. 3 coal.
- The efficacy of mixed solvents containing CS₂ and certain solvents (e.g., pyridine, dimethylsulfoxide, dimethylformamide) appears to be physical. The work to confirm more conclusively this hypothesis is in progress.

ACKNOWLEDGEMENT The work reported here was financially supported by the Department of Energy Contract No. DE-AC22-91PC91027.

REFERENCES

1. Sakurovs, R.; Lynch, L.J.; Barton, W.A. In *Coal Science II*; Schobert, H.H., Bartle, K.D., Lynch L.J., Ed.; ACS Symposium Series 461; ACS: Washington, DC, 1991; Chapter 9, p 111.
2. Iino, M.; Takanoashi, T.; Ohsuga, H.; Toda, K. *Fuel* **1988**, *67*, 1639.
3. Takanoashi, T.; Iino, M. *Energy Fuels* **1990**, *4*, 452.
4. Iino, M.; Matsuda, M. *Fuel* **1983**, *62*, 744.
5. Yun, Y.; Otake, Y.; Suuberg, E.M. *Prepr. Pap.- Am. Chem. Soc., Div. Fuel Chem.* **1991**, *36(3)*, 1314.
6. Suuberg, E.M.; Otake, Y.; Deevi, S.C. *Prepr. Pap.- Am. Chem. Soc., Div. Fuel Chem.* **1991**, *36(1)*, 258.
7. Vorres, K.S. *User's Handbook for the Argonne Premium Coal Sample Program*; Argonne, Illinois, 1989.
8. Meesiri, W.; Menczel, J.; Gaur, U.; Wunderlich, B. *J. of Polymer Science* **1982**, *20*, 719.
9. Petrucci, R.H. *General Chemistry*; The Macmillan Co.: New York, 1972.
10. Morrison, R.T.; Boyd, R.N. *Organic Chemistry*; Allyn and Bacon, Inc.: Boston, 1983.
11. Roberts, J.D.; Caserio, M.C. *Modern Organic Chemistry*; W.A. Benjamin, Inc.: New York, 1967.

Table 1. Volumetric Swelling Ratio by Mixed Solvents (1:1 v/v) for Upper Freeport Medium Volatile Bituminous Coal

Pretreatment	Solvent mixture (1:1 v/v)	Solvent characteristics			Q**
		Solvent	Acceptor Number	$\delta(H)^*$	
None	CS ₂ /pyridine	pyridine	14.2	10.4	1.95
	CS ₂ /dimethylsulfoxide	dimethylsulfoxide	19.3	12.8	1.75
	CS ₂ /dimethylformamide	dimethylformamide	16.0	11.5	1.92
	CS ₂ /n-butylamine	n-butylamine	-	-	1.21
	pyridine/water	water	-	9.4	1.08
	pyridine/methanol	methanol	41.3	12.9	1.09
	pyridine/chlorobenzene	chlorobenzene	-	9.5	1.12
	pyridine/chloroform	chloroform	-	9.3	1.13
	pyridine/methylene chloride	methylene chloride	-	9.7	1.14
	pyridine/nitroethane	nitroethane	-	11.1	1.09
Pyridine Soxhlet extracted	CS ₂ /pyridine	CS ₂	-	10.0	1.83
Acetylated	CS ₂ /pyridine	CS ₂	-	10.0	1.71

* δ : solubility parameter in Hildebrand which is equivalent to cal^{1/2}cm^{-3/2}

**Q: volumetric swelling ratio

Table 2. Solvent Swelling Results for Upper Freeport Medium Volatile Bituminous Coal

Pretreatment	Solvent	Solvent Properties				Q*	Swelling number** ($\times 10^3$)
		Donor No.	Acceptor No.	$\delta(H)^1$	Molar Vol.(cc/mol)		
None	pyridine	33.1	14.2	10.4	80.9	1.14	1.73
	CS ₂	-	-	10.0	60.3	1.08	1.33
	n-butylamine	-	-	-	99.8	1.12	1.20
	THF	20.0	8.0	9.1	81.1	1.08	0.99
	dimethylsulfoxide	29.8	19.3	12.8	71.0	1.09	1.27
	dimethylformamide	26.6	16.0	11.5	77.4	1.08	1.03
CS ₂ swelled	pyridine	33.1	14.2	10.4	80.9	1.12	1.48
Pyridine Soxhlet extracted	pyridine	33.1	14.2	10.4	80.9	1.19	2.35
	CS ₂	-	-	10.0	60.3	1.07	1.16
CS ₂ /pyridine (1:1 v/v) swelled	pyridine	33.1	14.2	10.4	80.9	1.40	4.94
	CS ₂	-	-	10.0	60.3	1.30	4.97
Heated under N ₂ up to 350°C	THF	20.0	8.0	9.1	81.1	1.82	10.11
	pyridine	33.1	14.2	10.4	80.9	2.17	14.46
	CS ₂	-	-	10.0	60.3	1.50	8.29
	dimethylsulfoxide	29.8	19.3	12.8	71.0	1.49	6.90
	chlorobenzene	-	-	9.5	101.7	1.40	3.93
CS ₂ /pyridine swelled and heated up to 350°C	pyridine	33.1	14.2	10.4	80.9	1.83	10.26
Acetylated	pyridine	33.1	14.2	10.4	80.9	1.10	1.24
	CS ₂	-	-	10.0	60.3	1.06	0.99

¹ δ : solubility parameter in Hildebrand which is equivalent to cal^{1/2}cm^{-3/2}

*Q: volumetric swelling ratio ** (Q-1)/molar volume

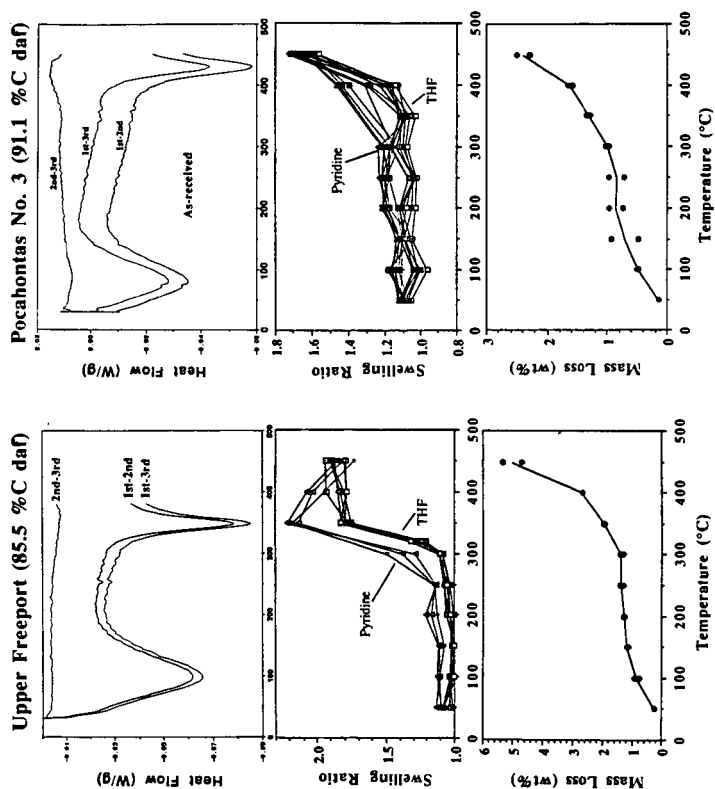


Figure 1. DSC difference thermograms as well as profiles of swelling ratio and weight loss for Upper Freeport (-100 mesh) and Pocahontas No. 3 (-20 mesh) coals. DSC was performed at 8°C/min under N₂ atmosphere.

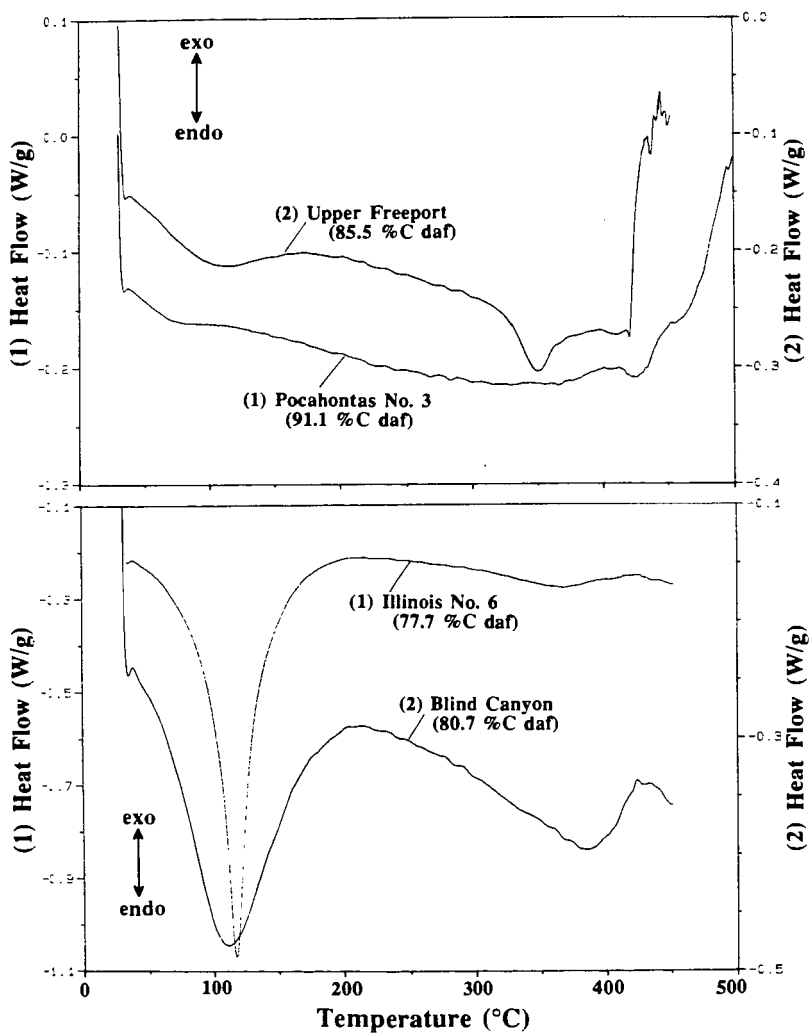


Figure 2. Comparison of DSC thermograms obtained at 8°C/min for different rank bituminous coals.

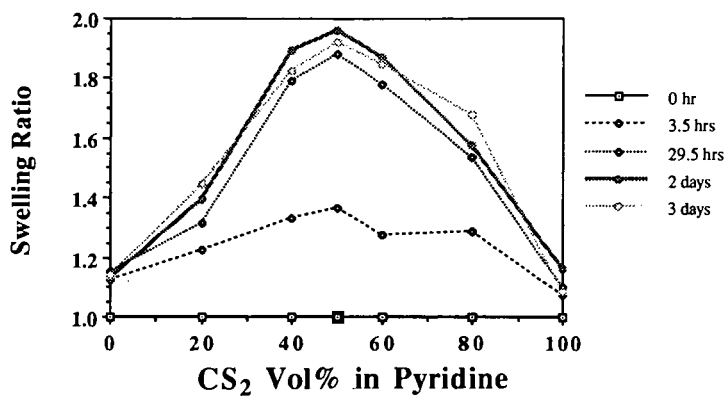


Figure 3. Changes of volumetric swelling ratio by mixed solvents of CS₂ and pyridine for Upper Freeport coal.

Table 3. Solvent Swelling Results for Pocahontas No. 3 Low Volatile Bituminous Coal

Pretreatment	Solvent	Q	Swelling number ($\times 10^3$)
None	pyridine	1.12	1.48
	CS ₂	1.16	2.65
	THF	1.10	1.23
	CS ₂ /pyridine (1:1 v/v)	1.16	-
CS ₂ swelled	pyridine	1.13	1.61
Heated under N ₂ up to 450°C	THF	1.65	8.01
	pyridine	1.72	8.90

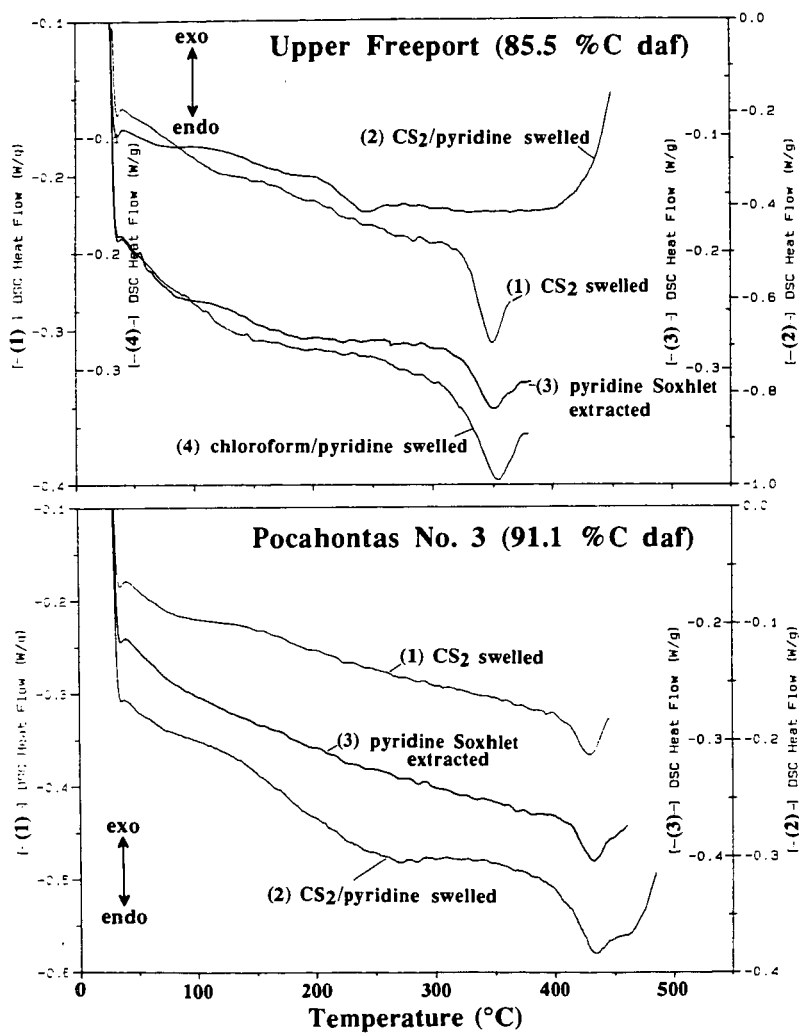


Figure 4. DSC thermograms obtained at 10°C/min for differently pretreated samples, illustrating the relaxed coal structure already at room temperature in CS₂/pyridine (1:1 v/v) swelled Upper Freeport Coal.